

# Protein induced self-assembly of GO

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Graphene has been acclaimed as a cutting edge material since its discovery [1]. Because of its noteworthy properties [2] it has attracted and is still attracting major interest. Moreover, graphene's benefits have further expanded after obtaining related materials such as graphene oxide (GO) [3] that features tunable electro-optical and chemical properties, high hydrophilicity and ease of production and functionalization. Yet the possibility of obtaining reduced GO (rGO) by processing contributed greatly to its outstanding potential, as rGO can partially restore the properties of graphene while enabling its dispersion in surfactant-free solution [4].

However, using graphene for practical applications remains to be fully realized. One main issue is the integration of its 2D structure into accessible and scalable 3D materials, a need that has inspired a growing field of research [5].

We accomplish the task of building 3D GO structures by Peroxiredoxins (Prx), a family of multi-tasking enzymes with ring-like architectures. Taking advantage of the proteins capabilities of interacting with both GO and rGO through weak interactions due to their exposed surfaces, as well as of their symmetric structure, 3D rGO-based composites are hereby built up.

The Prx rings adhere flat on single GO layers and induce partial reduction, driving their stacking into 3D multi-layer rGO-Prx composites, even when using very few amounts of GO. Further, protein engineering allows divalent metal ions to bind the Prx's lumen and this is exploited to capture pre-synthesized gold nanoparticles (AuNPs) and grow in situ palladium nanoparticles (PdNPs) using the protein ring as physical confinement, thus paving the way to straightforward and "green" routes to 3D rGO-metal composites.

GO quickly gets clumped in the presence of Prx during mixing experiments in solution. Such clumps progressively push together leading to a soft colloid which can be hanged as compact material. The colloid can form again even after breaking by shaking, hence suggesting that a reversible self-assembly process occurs. The so-formed rGO-Prx colloid can be easily dried as a free-standing material by freeze-drying while keeping a microporous internal architecture. Addition by protein engineering of metal-binding sites on the lumen of the Prx ring allows the protein to bind divalent metal ions. By this way, Prx can trap Ni(II)-functionalized AuNPs with ~2 nm diameter and carrier them inside the multi-layer rGO-based composite. The versatility of the system is also demonstrated for Pd(II) and for Co(II) [7].

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## References

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